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THE EFFECT OF ADDITIVES ON PROPERTIES OF CERAMICS BASED ON ZINC OXIDE

B. S. Skidan¹Translated from *Steklo i Keramika*, No. 10, pp. 35–37, October, 2003.

The results of the effect of some oxides on sintering and properties of ZnO-based ceramics are presented. Introduction of additives from respective salt solutions has the best effect on the formation of a ceramic microstructure. Ceramics in this case actively sinter according to the liquid-phase mechanism in the presence of glass-forming agents Bi₂O₃ and Sb₂O₃ and oxides of Ni, Mn, Sn, etc.

Varistors, or nonlinear resistors are acquiring wide application in electric engineering and electronics. They serve in devices using the voltage – strength of current functional dependence [1]. Zinc (zinc oxide) varistors are semiconductor resistors with a nonlinear volt-ampere characteristics (VAC). They have high ohmic resistance at low voltage and, vice versa, low resistance at high voltage. Volt-ampere characteristics are approximated by the equation:

$$I = BU^\beta,$$

where I is the strength of current, A; B is the constant for the particular material; U is voltage, V; β is the nonlinearity coefficient.

The behavior of a varistor is determined by its microstructure consisting of zinc oxide conducting grains surrounded by a thin (several nanometers) layer [1–4] enriched with the additive cations, which separates ZnO grains.

Usually varistors containing 85–99% ZnO (here and elsewhere molar content indicated) and the rest is represented by various admixtures introduced into ceramics by various methods and in different quantities. Each additive has a specific role in the formation of the structure and properties of the varistor.

As is noted in [5], varistors based on ZnO have typical characteristics of ceramics obtained by the liquid-phase sintering method. This ceramics consists of coarse ZnO grains surrounded by a vitreous phase up to 10^{-3} μm thick rich in Bi₂O₃ and containing crystallized secondary phases (spinel, pyrochlore, etc.). The VAC of these materials depends on the size of ZnO grains and also on the concentration and distribution of additives. A large size of ZnO grains leads to low working voltage on varistors, whereas a small

sizes leads to high voltage. Additives make it possible to control the growth of grains and develop a particular phase composition in the course of thermal treatment.

The most significant oxides determining electrophysical properties of zinc varistors are Bi₂O₃, Sb₂O₃, and Pr₂O₃, which form a liquid phase at relatively low temperatures (up to 1000°C) and control the growth of crystals and the density of materials at temperatures above 1100°C. The vitreous phase is mostly concentrated at the grain boundaries or in pores.

Small additives of NiO, CoO, and Cr₂O₃ in the presence of other additives increase the electric breakdown by decreasing the grain size, and Al₂O₃ decreases the porosity of materials.

The present study considered the effect of Bi₂O₃, CoO, MnO, and K₂O on ceramics containing over 99.5% ZnO oxide. Additives were introduced in the form of oxides and aqueous salt solutions for the purpose of a more homogenous distribution in the ceramic volume. The content of additives varied from 0.25 to 2.50%.

Oxide mixtures were molded by uniaxial compression in steel molds under pressure of 100 MPa. The samples were fired at 1150–1120°C with an exposure of 1–2 h.

The fired samples were analyzed with a microscope after preparing polished sections.

Samples of pure zinc oxide had low shrinkage (7%).

Zinc, bismuth, and cobalt oxides and silicon dioxide in the form of powders were mixed by joint milling for 3 min in a planetary mill in plastic drums using corundum balls with a ratio of material : balls equal to 1 : 4. Granulometric analysis revealed a decrease in the particle size from 20 to 2–5 μm . Samples molded and fired at 1200°C has substantial shrinkage (up to 15.5%). The method of mixture preparation (wet or dry) had virtually no effect on shrinkage. It was found that all mixtures sintered poorly at a temperature of 1150°C: the

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

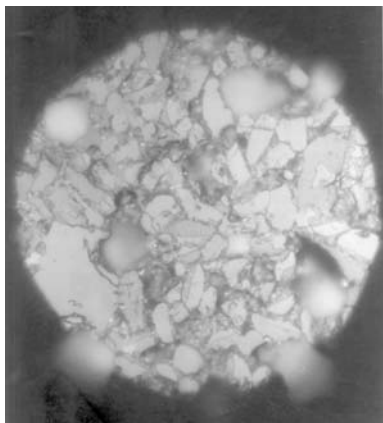


Fig. 1. Microstructure of ZnO ceramics with additives of CoO and SiO₂, 0.5% each ($\times 400$).

open porosity was 21–23% and mixtures without bismuth oxide had porosity of 31.5%. At 1200°C the open porosity decreased to 13–14% in all mixtures. This shows a significant effect of the firing temperature. An increase in a content of Bi₂O₃ from 1.0 to 2.5% made it possible to obtain material with zero open porosity and total porosity of 6.5–9.5%. Introduction of Bi₂O₃ in a mixture raises electric resistivity from 10^4 to $10^8 \Omega \cdot \text{cm}$. The nonlinearity coefficient in these samples does not exceed 3.

The size of zinc oxide crystals in the samples obtained was on the average 7–8 μm , reaching occasionally 50 μm . Two phases were clearly visible (Fig. 1). The second phase occupied part of the grain and had a clearly visible phase boundary. The pores were arranged along the grain boundaries (16–27 μm) and inside ZnO crystals (3–5 μm).

It was observed that open porosity was minimal with 0.25% K₂O (porosity 5.5%) with 0.25% CoO (porosity 2%). Analysis of the microstructure of samples revealed that the size of zinc oxide crystals ranges from 3–5 to 20 μm in samples containing 0.25 K₂O and is smaller (from 2–3 to 15 μm) in samples containing CoO. The pores are arranged along the grain boundaries and inside the grains.

Analysis of the effect of MnO additive established the optimum ceramics properties in a material containing 1.5% MnO. Porosity in this case reaches approximately 1%. The size of isometric zinc oxide crystals ranges from 3–7 to 15 μm .

The introduction of 0.5% Bi₂O₃ increases the size of isometric ZnO crystals from 5–15 to 35 μm .

The resistivity of ceramic samples with MnO and CoO additives that sinter according to the solid-phase mechanism was $10^8 - 10^6 \Omega \cdot \text{cm}$, and introducing Bi₂O₃ decreased resistivity to about $10^3 \Omega \cdot \text{cm}$.

The effect of Bi₂O₃ on sintering of ceramics was investigated within a content interval ranging from 1.0 to 2.5% with a variation step of 0.5%. The total porosity varied from 6.0 to

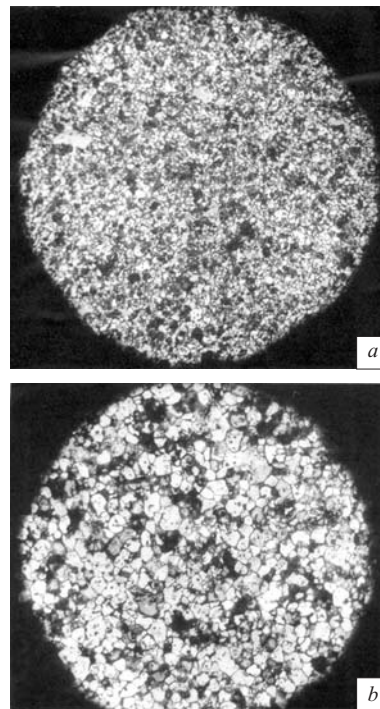


Fig. 2. Microstructure of ZnO ceramics with additives of 1% MnO (a) and MnO and Bi₂O₃ (b), 0.5% each ($\times 625$).

9.5% with an increasing content of Bi₂O₃. The size of ZnO crystals ranged from 5–10 to 50 μm .

To improve the distribution of additives, they were introduced in the form of aqueous solutions of respective salts, mixed with zinc oxide powder, and dried. The resulting powder was aggregated with a mean particles size of $d_m = 35 \mu\text{m}$. After dry milling in a planetary mill the powder had $d_m = 7 \mu\text{m}$. Further milling did not decrease the particle size, on the contrary, the powder became aggregated. Samples molded from this powder had substantial shrinkage (approximately 18%) with a 1.5% MnO content. A decrease in the concentration of MnO decreased shrinkage.

A simultaneous introduction of MnO and BiO led to high shrinkage as well (approximately 17.5%) and CoO mixed with Bi₂O₃ facilitated a somewhat lower shrinkage (approximately 16.7%). Despite substantial shrinkage in ceramics with 1.5% MnO, its open porosity was 0.5% and true porosity 9.5%. The introduction of 0.5% Bi₂O₃ caused an abrupt decrease in porosity to 0.4 and 4.8%, respectively. Cobalt oxide introduced into ZnO impairs sintering, but with additionally introduced bismuth oxide the effect is positive. Similarly to the case of MnO + Bi₂O₃, the microstructure of samples without Bi₂O₃ is represented by ZnO crystals of size 2–5 μm . An admixture of bismuth oxide makes crystals grow to 15 μm (Fig. 2).

Mixtures containing CoO had finer ZnO crystals than mixtures with MnO ($d_m \sim 10 \mu\text{m}$ against 13 μm). The resistivity of samples was about $10^3 \Omega \cdot \text{cm}$ with a bismuth oxide

additive and approximately $10^6 \Omega \cdot \text{cm}$ with MnO or CoO additives. The nonlinearity coefficient of such samples was insignificant.

The study of mixtures simultaneously containing oxides of bismuth, cobalt, antimony, and silicon indicated that Bi_2O_3 and Sb_2O_3 have a significant effect of the VAC and presumably act as low-temperature glass-forming agents. Elimination of one or another component decreases the nonlinearity coefficient from 12–13 to 2–4 and leads to a sharp growth of ZnO crystals from 5–10 to 20–40 μm . It should be noted that the material had two phases and the second phase took about half of the crystal with a clearly defined phase boundary.

The powders obtained by coprecipitation from aqueous salts of Zn, Bi, Co, and Mn (oxalic acid acting as precipitator) were highly aggregated, therefore, they were milled to $d_m \sim 10 \mu\text{m}$. Fired samples had open porosity from 21 to 38% with the content of bismuth oxide varying from 0 to 2%. Adding CoO and MnO, 0.5% or 0.25% each, to a mixture containing 0.5% Bi_2O_3 significantly improved its sintering: the open porosity was about 3% and the total porosity 8–10%. The resistivity varied from 10^5 – $10^6 \Omega \cdot \text{cm}$ with the bismuth oxide additive to $10^9 \Omega \cdot \text{cm}$ on introducing MnO and CoO. The size of ZnO crystals was 8–13 μm . It should be noted that the material had two phases. The second phase (gray color) was present as well in the form of well-edged crystals of a similar size separated by ZnO crystals.

It should be noted that introduction of Bi_2O_3 and Sb_2O_3 together with MnO, CoO and other additives facilitates sintering.

The method of mixture preparation has a great effect on sintering and homogeneity of materials. In chemical coprecipitation, the growth of ZnO crystals is delayed and a homogeneous structure with a clearly defined phase boundary is formed. The introduction of 0.5% Bi_2O_3 and CoO or MnO leads to a sharp decrease in total (to 8–11%) and open (to about 3%) porosity. In the case of using a mixture of oxides (0.5% Bi_2O_3 , 0.25% CoO, and 0.25% MnO), a similar effect was observed.

It was found that ZnO crystals with Bi_2O_3 additives have an average size about 30 μm . Adding MnO decreases this size to about 20 μm , and adding CoO decreases it to 15 μm .

The size of the pores located at the boundary between three crystals reaches 15 μm , and the size of the pores inside the crystals is about 2 μm .

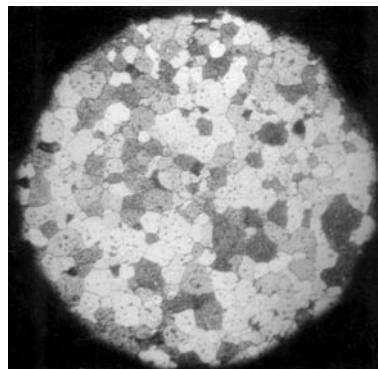


Fig. 3. Microstructure of ZnO ceramics with additives of Bi_2O_3 and MnO, 0.5% each ($\times 400$).

With simultaneous introduction of CoO and MnO, a homogeneous structure with finer crystals (about 10 μm) was obtained.

In working with ZnO, it was observed that initial dispersion of powder affects sintering. Thus, zinc oxide of grade “analytically pure” consists of aggregates sized up to 100 μm that are hard to mill, therefore, samples cannot be sintered to high density. Ceramics with Bi_2O_3 , CoO, MnO, TiO_2 , and SnO_2 additives sintered to a minimum porosity (6%) at 1200°C. The volt-ampere characteristics of ceramics based on ZnO of grades “pure” and “chemically pure” were in the limits of 17–22 and that of the “analytically pure” grade was about 3.

Thus, introduction of manganese, cobalt and other oxide additives in the presence of bismuth and antimony oxides improves sintering of ZnO-based ceramics. The method of mixture preparation has a significant effect on sintering and homogeneity of material.

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